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(54) **Composite substrate for fuel cells and process for producing the same**

(57) Disclosed herein is a composite substrate for fuel cells, comprising (1) a separator, (2) two porous and carbonaceous electrode substrates which are joined to the separator, respectively provided with a plurality of grooves forming the flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof and (3) peripheral sealers which have been joined to the separator via a layer of a fluorocarbon resin, the above-mentioned electrode substrates having been joined to the opposing surfaces of the above-mentioned separator so that the flow channels of the reactant gas in one of the electrode substrates are perpendicular to those in the another electrode substrate, a ratio of the sum of the cross-sectional areas of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the fuel electrode side to the sum of the cross-sectional areas of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the air electrode side being from 1:3 to 2:3, and a process for producing the above-mentioned composite substrate for fuel cells.

Fig.1

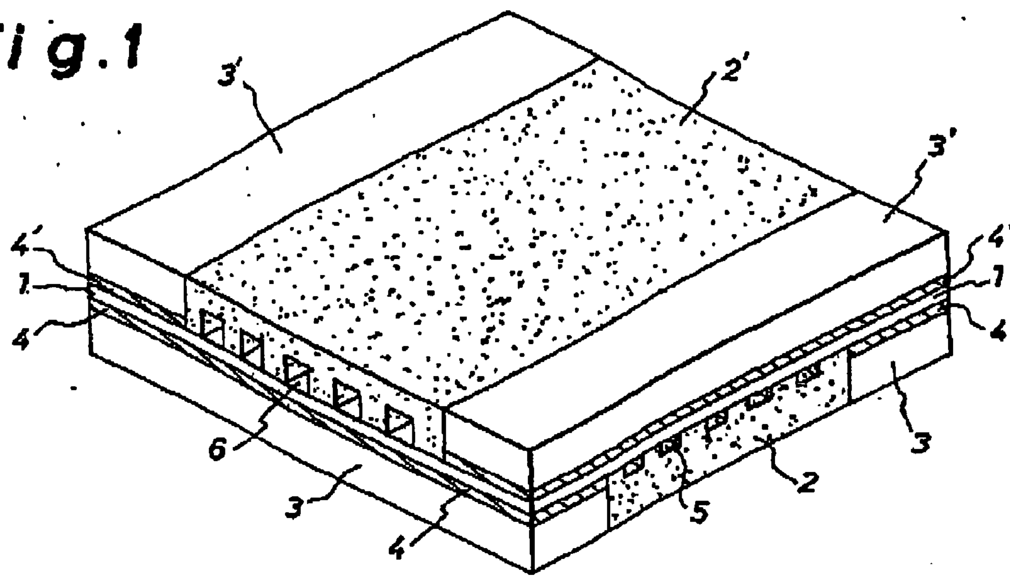

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Fig.1

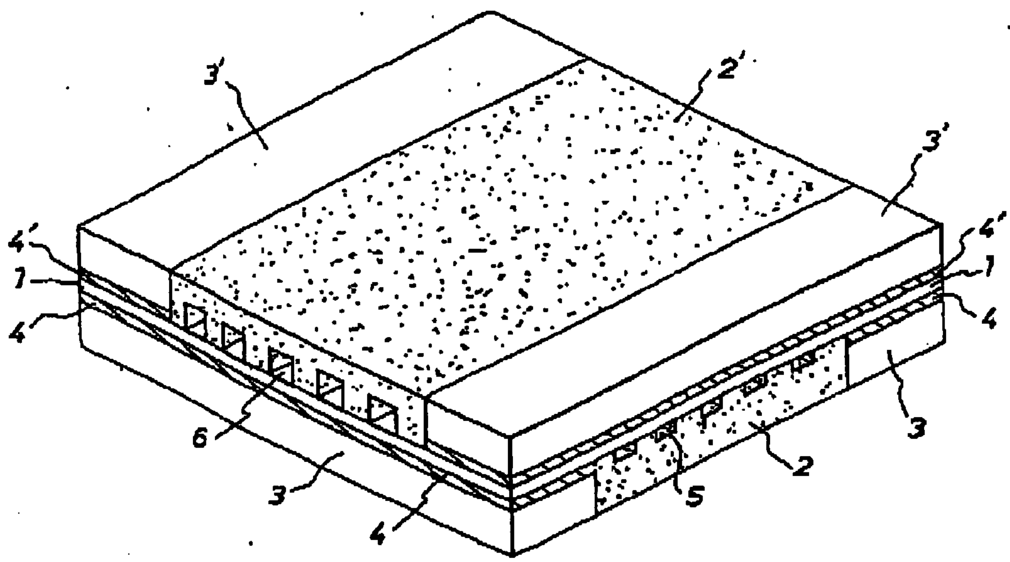

Fig.2

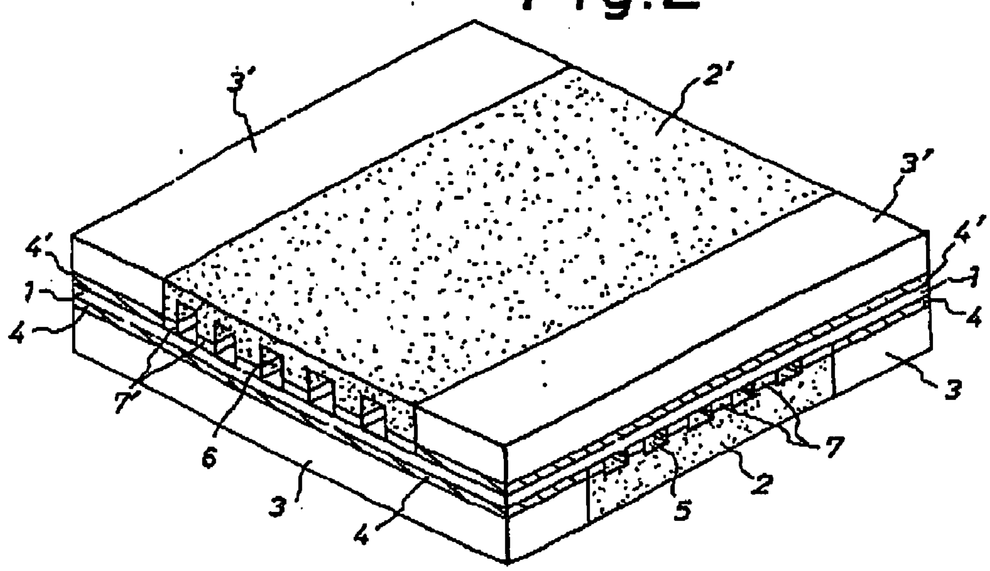

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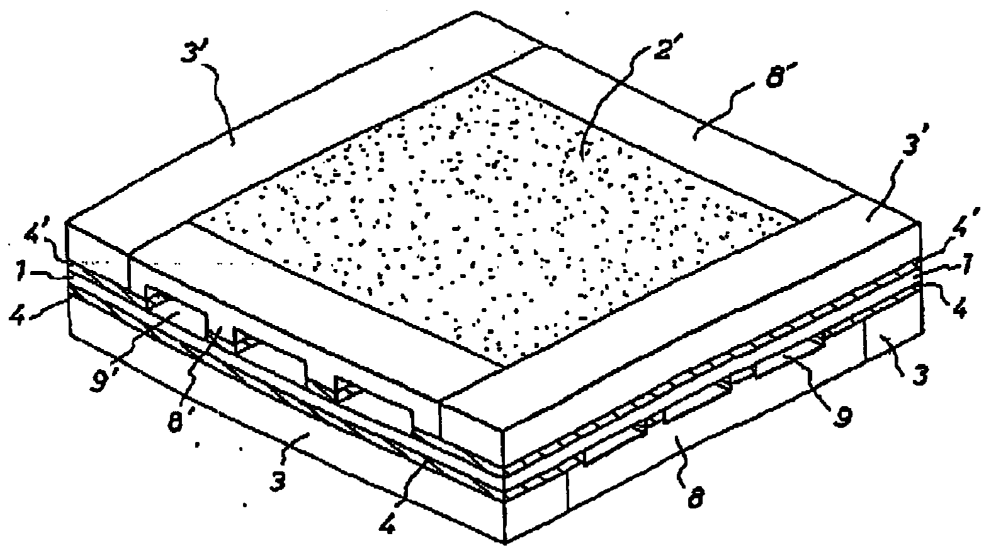
Fig.3



the fuel electrode side and (2) the leakage of the gas to the side of the electrode can be prevented by joining peripheral sealers to the separator via a layer of a fluorocarbon resin, and on the basis of their findings, the present inventors have attained the present invention.

Namely, the first object of the present invention is to provide a composite substrate for fuel cells, which comprises a separator, two porous and carbonaceous electrode substrates and peripheral sealers and has a ratio of the cross-sectional area of the flow channel of the reactant gas on the fuel electrode side to that on the air electrode side, which ratio is in conformity to the conditions of the actually used fuel.

Furthermore, the second object of the present invention is to provide a composite substrate for fuel cells wherein the edge of the porous and carbonaceous electrode substrate has been sealed by joining peripheral sealers to extended peripheries of the separator via a layer of a fluorocarbon resin, thereby not necessitating the peripheral sealing treatment for preventing the leakage of the reactant gas to the side of the cell.

The third object of the present invention is to provide a composite substrate for fuel cell of phosphoric acid tYpe, which is excellent in resistance to phosphoric acid.

SUMMARY OF THE INVENTION:

In a first aspect of the present invention, there is provided a composite substrate for fuel cells, comprising

(1) a separator,

(2) two porous and carbonaceous electrode substrates which have been respectively provided with a plurality of grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof and have been joined to opposing surfaces of the separator so that the flow channels of the reactant gas in one of the electrode substrates are perpendicular to those in the another electrode substrate and the separator extends beyond both edges of the electrode substrate that are parallel to the flow channels of the reactant gas in the electrode substrate and

(3) peripheral sealers joined to the extended peripheries of the separator, which extend beyond the both edges of the electrode substrate, via a layer of a fluorocarbon resin,

a ratio of the sum of the cross-sectional area of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the air electrode side being from 1:3 to 2:3.

In a second aspect of the present invention, there is provided a process for producing a composite substrate for fuel cells, which process comprises the steps of

(1) adhering a flexible carbon sheet to one surface of each of two porous and carbonaceous electrode substrates of a flat plate form without grooves and of prescribed dimension while using an adhesive,

(2) subjecting each of the adhering surfaces of said electrode substrates to cut-processing to form grooves forming flow channels of the reactant gas thereon so that a ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3,

(3) adhering the surfaces of the flexible carbon sheet remaining on the thus cut-processed surfaces of the electrode substrates to opposing surfaces of the separator so that the grooves in one of the electrode substrate are perpendicular to those in the another electrode substrate,

(4) calcining the thus adhered materials at a temperature of not lower than about 800°C in an inert atmosphere and/or under a reduced pressure, and

(5) joining peripheral sealers comprising a gasimpermeable compact carbon material to extended peripheries of the separator, which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein, via a sheet of a fluorocarbon resin.

In a third aspect of the present invention, there is provided a process for producing a composite substrate for fuel cells, which process comprises the steps of

(1) applying a dispersion of a tetrafluoroethylene resin on opposing surfaces of a separator,

(2) joining by melt-adhesion each of grooved surfaces of two porous and carbonaceous electrode substrates to the prescribed position of the opposing surfaces of the separator applied with the dispersion so that the grooves in one of the electrode substrates are perpendicular to those in the another electrode substrate, the electrode substrates being respectively provided with a plurality of the grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof, the size of the grooves being such that a ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3, and

(3) joining peripheral sealers comprising a gasimpermeable compact carbon material to extended peripheries of the separator which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the the reactant gas therein, via a sheet of a fluorocarbon resin.

BRIEF EXPLANATION OF THE DRAWINGS:

Of the attached drawings, Figs. 1 to 3 are the oblique views of the composite substrate according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention relates to a bipolar-type composite substrate for fuel cells, which substrate comprises a separator, two Porous and carbonaceous electrode substrates forming a fuel (hydrogen) electrode and an air electrode while interposing the separator therebetween and peripheral sealers, and a process for producing the composite substrate for fuel cells.

As has been described, the stoichiometrical ratio by volume of fuel (hydrogen) to oxygen in a fuel cell of phosphoric acid type is 2:1. In the actual operation of a fuel cell, since oxygen is supplied by air, the content of oxygen in the thus supplied gas is about 20 %, and the gas for supplying hydrogen is, as has been described above, a reformed LNG, LPG, etc. containing CO_2, water vapour, etc., and has the content of hydrogen of from about 65 to about 80 % by volume.

On the other hand, concerning the rate of utilization represented by the ratio of the amount of the consumed reactant gas to that of the supplied reactant gas, since the terminal voltage of the cell begins to go down in the case where the above-mentioned rate of utilization exceeds a definite value, the rate of utilization is limited. In practice, it is necessary that the rate of utilization of hydrogen is not more than 75 % and that the rate of utilization of oxygen is not more than 50 %.

In the case of carrying out the calculation provided that the two reactant gases are used under the same pressure, the ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side becomes to about from 0.325 : 1 to 0.41 : 1, and in consideration that the content of hydrogen may be a little smaller according to the conditions of the hydrogen-supplying gas, the above-mentioned ratio of the sum of from about 1:3 to about 2:3 can agree with the actual conditions of supplying gases.

Further, in the case of joining the electrode substrate to the separator by adhering both the materials to each other with a carbonizable adhesive and calcining the thus adhered materials into one body or adhering both the materials to each other with a dispersion of a tetrafluoroethylene resin, sufficient electrical characteristics and resistance to phosphoric acid can be obtained in the product, and in the case where the peripheral sealers of the compact carbon material is joined to the separator via a sheet of a fluorocarbon resin, a sufficient prevention of gas-leakage, a resistance to phosphoric acid and the over-all mechanical strength can be obtained in the product.

The present invention offers a composite substrate for fuel cells, comprisising (1) a separator, (2) two porous and carbonaceous electrode substrates which have been respectively provided with a plurality of grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof and have been joined to opposing surfaces of the separator so that the flow channels of the reactant gas in one of the electrode substrates are perpendicular to those in the another electrode substrate and the separator extends beyond both edges of the electrode substrate that are parallel to the flow channels of the reactant gas in the electrode substrate and (3) peripheral sealers joined to the extended peripheries of the separator, which extend beyond the both edges of the electrode substrate, via a layer of a fluorocarbon resin, a ratio of the sum of the cross-sectional area of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas formed by the separator and the grooves of the porous and carbonaceous electrode substrate on the air electrode side being from 1:3 to 2:3. Furthermore, the cross-sectional area of the flow channels of the reactant gas mentioned in the present invention indicates the sectional area of the flow channel of the reactant gas, which section is orthogonal to the flow direction of the reactant gas.

In the composite substrate for fuel cells according to the present invention, the porous and carbonaceous electrode substrates and the separator may be joined together by calcining into one body after being adhered to each other by a carbonizable adhesive, or may be joined together by using a dispersion of a tetrafluoroethylene resin. In the case of carrying out the joining by calcination into one body, it is desirable to interpose a flexible carbon sheet between the materials, as the buffer sheet absorbing the thermal expansion and shrinkage of the materials at the time of calcination.

Accordingly, the present invention also offers a process for producing the above-mentioned composite substrate for fuel cells, which process comprises the steps of (1) adhering a flexible carbon sheet to one surface of each of two porous and carbonaceous electrode substrates of a flat plate form without grooves and of prescribed dimension while using an adhesive, (2) subjecting each of the adhering surfaces of said electrode substrates to cut-processing to form grooves forming flow channels of the reactant gas thereon so that a ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3, (3) adhering the surfaces of the flexible carbon sheet remaining on the thus cut-processed surfaces of the electrode substrates to opposing surfaces of the separator so that the grooves in one of the electrode substrates are perpendicular to those in the another electrode substrate, (4) calcining the thus adhered materials at a temperature of not lower than about 800°C in an inert atmosphere and/or under a reduced pressure, and (5) joining peripheral sealers comprising a gas-impermeable compact carbon material to extended peripheries of the separator, which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein, via a sheet of a fluorocarbon resin.

Further, the present invention offers a process for producing the above-mentioned composite substrate for fuel cells, which process comprises the steps of (1) applying a dispersion of a tetrafluoroethylene resin on opposing surfaces of a separator, (2) joining by melt-adhesion each of grooved surfaces of two porous and carbonaceous electrode substrates to the prescribed position of the opposing surfaces of the separator applied with the dispersion so that the grooves in one of the electrode substrates are perpendicular to those in the another electrode substrate, the electrode substrates being respectively provided with a plurality of the grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof, the size of the grooves being such that a ratio of the sum of the crosssectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3, and (3) joining peripheral sealers comprising a gas-impermeable compact carbon material to extended peripheries of the separator which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein, via a sheet of a fluorocarbon resin.

The composite substrate according to the present invention will be explained more in detail while referring to the attached drawings.

Of the attached drawings, Fig. 1 is the oblique view of the composite substrate according to the present invention, wherein two porous and carbonaceous electrode substrates and a separator have been joined together by a dispersion of a tetrafluoroethylene resin.

The composite substrate of Fig. 1 according to the present invention has a structure consisting of a separator *1*, two electrode substrates, i.e., the electrode substrate for the fuel electrode *2* and the electrode substrate for the air electrode *2'*, which respectively have grooves forming flow channels *5* and *6* of the reactant gas together with the above-mentioned separator and are situated on opposing surfaces of the separator and peripheral sealers *3* and *3'* which seal both edges of the electrode substrates *2* and *2'*, which edges are parallel to the direction of the flow channels *5* and *6* of the reactant gas.

The area of the separator *1* is larger than that of the electrode substrates *2* and *2'*, and as is shown in Fig. 1, the separator *1* extends beyond both edges of the electrode substrate that are parallel to the flow channels *5* and *6* of the reactant gas in the electrode substrate, and the peripheral sealers *3* and *3'* are joined to the abovementioned extended peripheries of the separator *1* (the outer edge of the extended peripheries of the above-mentioned separator coincided with the outer edge of the peripheral sealers).

The extended peripheries of the separator, which extend beyond the both edges of the electrode substrate and the peripheral sealers *3* and *3'* have been joined together via fluorocarbon resins *4* and *4'*, respectively.

In the composite substrate shown in Fig. 1, the separator *1* and the electrode substrates *2* and *2'* have been joined together by a dispersion of a tetrafluoroethylene resin, and the flow channels *5* and *6* of the reactant gas are prescribed by the grooves of the electrode substrates *2* and *2'* and the separator.

Further, Fig. 2 shows the composite substrate formed by joining the separator *1* and the electrode substrates *2* and *2'* together while interposing each of flexible carbon sheets *7* and *7'* between the separator and each of the electrode substrates *2* and *2'*.

In the composite substrate according to the present invention shown in Figs. 1 and 2, the ratio of the sum of the cross-sectional area of the flow channels *5* of the reactant gas on the fuel electrode side to the sum of the crosssectional area of the flow channels *6* of the reactant gas on the air electrode side is from 1:3 to 2:3. The shape of the cross-section of the flow channels of the reactant gas, which fulfills the above-mentioned ratio of the cross-sectional area may be made optional. However, from the view point of the effect of possibly making the

thickness of the electrode substrate itself thinner and improving the performance and mechanical strength of the cell itself, it is desirable that the flow channels of the reactant gas are generally formed in a rectangular form, and the cross-sectional areas of the flow channels of the reactant gas on the both electrode sides are different by providing the flow channels of the reactant gas with the same width on the fuel electrode side and on the air electrode side and providing the flow channels of the reactant gas with the different height between the fuel electrode side and the air electrode side (i.e., the depth of the grooves of the electrode substrate is different between the fuel electrode side and the air electrode side).

The shape of the cross-section of the flow channels of the reactant gas, which is shown in Figs. 1 and 2, is rectangular and the flow channels of the reactant gas extend in parallel with the sealed edge and linearly from one of the open ends to the other thereof, however, in the case where the flow channel of the reactant gas can sufficiently supply the reactant gas which diffuses into the porous and carbonaceous electrode substrates, the cross-section of the flow channels of the reactant gas may take any optional shape. For instance, in the case where the cross-section of the ribs which form the grooves of the electrode substrate takes a shape of a trapezoid or a non-linear shape, it is possible to aim at the dispersion of the stress on the electrode substrates and such a situation is particularly favorable at the time of producing the composite substrate. Furthermore, it is also possible to connect the flow channels of the reactant gas together within the electrode substrate, and the protuberant parts having top surfaces which become joining surfaces to the separator and have the optional shape such as circle, ellipse, rectangle, etc., may be disposed on the joining surface side of the electrode substrate to be joined to the separator in series, entangled positions or in any optional positions. Of course, any combination of the above-mentioned shapes and dispositions may be possible.

The electrode substrate of the present invention is porous and carbonaceous, and it is favorable that the electrode substrate has the properties of a mean bulk density of from 0.3 to 0.9 g/ml, a gas-permeability of not less than 200 ml/cm^2·hour·mmAq and an electric resistivity of not more than 200 mΩ·cm after being calcined at a temperature of not lower than 800°C in an inert atmosphere and/or under a reduced pressure.

It is favorable that the separator used according to the present invention has the properties of a mean bulk density of not less than 1.4 g/ml, a gas-permeability of not more than 10^{-6} ml/cm^2·hour·mmAq, an electric resistivity of not more than 10 mΩ·cm and a thickness of not more than 2 mm.

It is favorable that the peripheral sealers used according to the present invention has the properties of a mean bulk density of not less than 1.4 g/ml and a gaspermeability of not more than 10^{-4} ml/cm^2·hour·mmAq.

As has been described above, in the composite substrate for fuel cells according to the present invention, although the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein, are sealed by joining the peripheral sealers comprising the compact carbon material to the separator via the sheet of a fluorocarbon resin, the amount of gas leakage to outside through the peripheral sealers including the joining part is mainly subjected to diffusion and is not affected so much by the pressure, however, in the present invention, it is favorable that the amount of gas leakage is not more than 10^{-2} ml/cm·hour·mmAq in the case where the amount of gas leakage per unit time and per the unit length of the peripheral side of the joining part under a differential pressure of 500 mmAq is represented by [the amount of gas leakage/length of the side.differential pressure].

The fluorocarbon resin used for joining the peripheral sealers to the extended peripheries of the separator according to the present invention is generally a fluorocarbon resin of a melting point of not lower than 200°C, and although such a resin is not particularly limited, for instance, tetrafluoroethylene resin (referred to PTFE of the melting point of 327°C and the thermal deforming temperature of 121°C under 4.6 kgf*/cm^{2}G), copolymer resin of tetrafluoroethylene and hexafluoropropylene (referred to FEP of a melting point of from 250 to 280°C and the thermal deforming temperature of 72°C under 4.6 kgf*/cm^{2}G), fluorinated alkoxyethylene resin (referred to PFA of a melting point of from 300 to 310°C and the thermal deforming temperature of 75°C under 4.6 kgf*/cm^{2}G) and fluorinated copolymer resin of ethylene and propylene (referred to as TFP of a melting point of from 290 to 300°C) may be exemplified. The above-mentioned fluorocarbon resins have been commercialized. Of the above-mentioned fluorocarbon resins, tetrafluoroethylene resin is preferable and is commercialized under the registered trade name of TEFLON®.

In the present invention, it is desirable to use the above-mentioned fluorocarbon resin as, for instance, a sheet of a thickness of about 50 micrometers.

As the electrode substrade of the composite substrate of the present invention, the following materials are used:

(1) The material made by molding a mixture of short carbon fibers, a binder and an organic granular substance by heating under a pressure (for instance, refer to U.S. Patent No.

4,522,895).

Particularly favorable is the material made by molding a mixture consisting of from 20 to 60 % by weight of short carbon fibers of a diameter of 5 to 30 μm, a length of 0.05 to 2 mm and a linear carbonizing shrinkage on calcining thereof at 2000°C of 0.1 to 3.0 %, from 20 to 50 % by weight of a carbonaceous binder of a carbonizing yield of 30 to 75 % by weight such as phenol resin, epoxy resin and petroleum and/or coal pitch and from 20 to 50 % by weight of an organic granular substances (a micro pore-regulator and a molding agent) having a carbonizing yield of at most 30 % by weight, diameter of 30 to 300 μm and do not evaporate at 100°C such as polyvinyl alcohol, polyethylene, polypropylene, polyvinyl chloride, copolymer resin of ethylene and vinylacetate and sugar or a mixture thereof under conditions of a molding temperature of from 100 to 180°C, a molding pressure of from 2 to 100 kgf*/cm²G and a pressure-retention time of from 1 to 60 min., and

(2) The material made by calcining the above-mentioned material of the above (1) at a temperature of not lower than 800°C in an inert atmosphere and/or under a reduced pressure.

However, in the case where the separator and the electrode substrate are joined together by a dispersion of a tetrafluoroethylene resin, the material which has been calcined, i.e., the material of the above (2) is used.

As the separator used according to the present invention, a compact carbon plate showing a calcining shrinkage of not larger than 0.2 % when it is calcined at 2000°C in an inert atmosphere and/or under a reduced pressure is favorable.

In the following, the materials used for producing the composite substrate of the present invention prepared by adhering a separator and electrode substrates together via a flexible carbon sheet interposed between the joining surfaces of the electrode substrate and the separator while using an adhesive and calcining the thus adhered materials into one body, and the process for producing the composite substrate of the present invention are described.

As the flexible carbon sheet used according to the present invention, a flexible graphite sheet made by compressing expanded granules of graphite obtained by subjecting granules of graphite of a particle diameter of not more than 5 mm to acid-treatment and further heating the thus acid-treated granules is mentioned. It is favorable that the thus produced flexible graphite sheet is not more than 1 mm in thickness and shows the properties of a bulk density of from 1.0 to 1.5 g/ml, a compression strain rate (i.e., the rate of strain under a compression load of 1 kgf*/cm²) of not more than 0.35 × 10⁻² cm²kgf* and a flexibility of not being broken in the case where it is bent to the radius of curvature of 20 mm. Of the commercialized flexible graphite sheets, GRAFOIL® (made by U.C.C.) is a suitable example.

Furthermore, as the flexible carbon sheet also used according to the present invention, the following material may be used:

A composite material prepared by mixing carbon fibers of a diameter of 4 to 25 μm and a mean length of not less than 1 mm which have been obtained by thermally treating polyacrylonitrile, rayon, phenol resin, isotropic pitch or anisotropic pitch at a temperature of not less than 1000°C and a binder of a carbonizing yield of not less than 10 % by weight such as one material selected from the group consisting of phenol resins, epoxy resins, furan resins, pitches of petroleum or coal series, polyvinyl alcohols, polyvinyl chlorides, polyacrylonitriles, rayons and polymers of siloxane, or a composite material prepared by pouring the binder into a matrix of carbon fibers is molded by heating under a pressure and the thus molded composite material is calcined at a temperature of not lower than 850°C in an inert atmosphere and/or under a reduced pressure to obtain the flexible carbon sheet. In the thus produced flexible carbon sheet, the carbon lumps derived from the binder are dispersed in the matrix of carbon fibers and restrain a plurality of carbon fibers, and the carbon fibers are slidably held to one another by the carbon lumps. Such a flexible carbon sheet has the properties of a thickness of not more than 1 mm, a bulk density of from 0.2 to 1.3 g/ml and a compression strain rate of not more than 2.0 × 10⁻¹ cm²/kgf;* The above-mentioned flexible carbon sheet has a flexibility of not being broken in the case where it is bent to the radius of curvature of 10 mm.

As the adhesive used in each of the adhering surfaces in the case of joining the electrode substrates and the separator via the flexible carbon sheet, any adhesive generally used in adhesion of the carbon materials may be used, however, particularly, a thermosetting resin selected from the group consisting of phenol resins, epoxy resins and furan resins is preferable.

Although the thickness of the layer of the abovementioned adhesive is not particularly limited, it is generally favorable to apply the adhesive uniformly in the thickness of not more than 0.5 mm.

Furthermore, the adhesion by the above-mentioned adhesive may be carried out at a temperature of from 100 to 180°C, under a press-pressure of from 1 to 50 kgf*/cm²G for a press-time period in a range of from 1 to 120 min.

The composite material prepared by adhering the flexible carbon sheet to the two electrode substrates while using the above-mentioned adhesive and the above-mentioned conditions of adhering is processed as follows.

Namely, the surface of the electrode substrate, to which the carbon sheet has been adhered, is subjected to cut-processing for providing grooves of a desired size which form the flow channels of the reactant gas so that the ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3. The above-mentioned cut-processing may be carried out by any optional means, for instance, the cut-processing is carried out by using a diamond blade.

The surfaces of the two flexible carbon sheets remaining on the thus cut-processed electrode substrates are adhered to the opposing surfaces of the separator as in the case of adhering the above-mentioned electrode substrates to the carbon sheet and the thus combined material is calcined at a temperature of not lower than about 800°C in an inert atmosphere and/or under a reduced pressure. The carbonization of the thus combined materials can be ensured by carrying out the same calcination after adhering the electrode substrates to the carbon sheet in the same manner as the calcination before the cut-processing. Namely, calcination is carried out two times.

Thereafter, the peripheral sealers comprising a gas-impermeable compact carbon material are joined by melt-adhesion of a sheet of a fluorocarbon resin (namely, via the sheet of the fluorocarbon resin) to the extended peripheries of the separator, which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein and are adjacent to the both edges of the above-mentioned electrode substrate, at a temperature of not lower than the temperature of lower than the melting point of the fluorocarbon resin by 50°C under a pressure of not lower than 1 kgf*/cm²G, the sheet of the fluorocarbon resin having been previously interposed between each of the peripheral sealers and each of the extended peripheries.

In order to obtain the structure of the above-mentioned electrode substrate according to the present invention, for instance, several modified methods can be taken. For instance, the flexible carbon sheet is joined to the upper surface of the protuberance formed after providing the grooves on the electrode substrate by cut-processing. However, it is most practical to carry out the cut-processing after joining the flexible carbon sheet onto the electrode substrate which has not yet been subjected to cut-processing.

Furthermore, in certain circumstances of production, the flexible carbon sheets *7* and *7'* may be the same size as the electrode substrate, and may be joined to the whole surface of the separator. Such an embodiment is in the scope of the present invention. However, from the view point of the thickness of the composite substrate, since the former structure is able to reduce the thickness of the composite substrate than the latter structure by the thickness of the flexible carbon sheet while maintaining the same cross-sectional area of the flow channels of the reactant gas, the former structure is preferable.

In the next place, the materials for use in producing the composite substrate, wherein the separator and the electrode substrates are joined together by a dispersion of a tetrafluoroethylene resin and the process for producing such a composite substrate are described.

As the dispersion of a tetrafluoroethylene resin, an aqueous dispersion containing from 10 to 70 % by weight, for instance, about 60 % by weight of the above-mentioned tetrafluoroethylene resin is used. It is possible to add a small amount of a surfactant to the above-mentioned dispersion.

After applying the above-mentioned dispersion of a tetrafluoroethylene resin on the opposing surfaces of the separator at the thickness of from 0.01 to 0.5 mm, the grooved surfaces of the two electrode substrates, on which the grooves have been formed preliminarily in order to form the flow channels of the reactant gas so that the ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3, are brought into face to face to the opposing surfaces of the separator and they are joined by melt adhesion at a temperature of not lower than about 270°C under a pressure of not less than 1 kgf*/cm²G.

In this connection, although the tetrafluoroethylene resin is a non-electroconductive substance, the electroconductivity between the porous and carbonaceous electrode substrate and the separator is sufficiently secured. The reason thereof is considered as follows. Since at the time of the above-mentioned adhesion under a pressure, the two materials are joined together so that the tetrafluoroethylene resin applied onto the separator is impregnated into the porous and carbonaceous electrode substrate, the two materials are joined together with a sufficient strength and at the same time, the contact of the two materials is sufficiently secured.

Thereafter, the peripheral sealers comprising a gas-impermeable compact carbon material is joined by melt-adhesion of a sheet of a fluorocarbon resin (namely, via the sheet of the fluorocarbon resin) to the extended peripheries of the separator, which extend beyond the both edges of the electrode substrate that are parallel to the flow channels of the reactant gas therein and which are adjacent to the both edges of the above-mentioned electrode substrate, in the same manner as mentioned above, the sheet of the fluorocarbon resin having previously inter-

posed between each of the peripheral sealers and each of the extended peripheries.

The afore-mentioned joining of the porous and carbonaceous electrode substrates and the separator and the joining of the separator and the peripheral sealers via the above-mentioned sheet of a fluorocarbon resin can be carried out at the same time by selecting the joining conditions suitably, and such an operation is particularly advantageous, because the number of the steps can be reduced by such an operation.

The molding of the porous and carbonaceous electrode substrate having the grooves forming the flow channels of the reactant gas can be carried out by any optional method. For instance, after filling the mixture of raw materials into a metal mold of a desired shape, the thus filled mixture is press-molded, or after molding the mixture of raw materials into a flat plate form (after further calcining the molded mixture), the grooves are formed by cut-processing. However, from the view point of the productivity and the uniformity of the products, it is desirable to extrude the mixture of raw materials after kneading thereof and then to press-mold the thus extruded mixture by rolling or stamping.

Furthermore, the composite substrate according to the present invention may have, as is shown in Fig. 3, the gas-distributors 8 and 8' which are made of the same compact carbon material as in the peripheral sealers and are disposed so as to be adjacent to the both edges of the electrode substrate that are perpendicular to the flow channels of the reactant gas therein.

The above-mentioned gas-distributors 8 and 8' have the grooves which form the flow passages for distributing the reactant gas together with the separator, and through the above-mentioned flow passages 9 and 9' for distributing the reactant gas, the reactant gas is supplied from outside to the flow channels 5 and 6 of the reactant gas (not shown in Fig. 3), however, it is not necessary that the cross-sectional shape of the flow passages 9 and 9' coincides with the crosssectional shape of the flow channels 5 and 6 of the reactant gas, and furthermore, it is also not necessary that all of the open ends of the flow channels 5 and 6 of the reactant gas are opened to the flow passages 9 and 9' for distributing the reactant gas, and the cross-sectional shape of the flow passages 9 and 9' for distributing the reactant gas may be such that the necessary amount of the flux of the reactant gas is secured when the apparatus is used as the composite substrate for fuel cells.

Concerning the cross-sectional area of the flow passages 9 and 9' for distributing the reactant gas, it is not necessary to provide the other conditions than the abovementioned, and accordingly, it is only required that the ratio of the sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of the flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3.

Further, in the composite substrate shown in Fig. 3, since the peripheral sealer and the gas-distributor both of which have been formed of the same material are opposite each other across the separator and the thermal expansion coefficient of the upper layer coincides with that of the lower layer, the thermal stress between the separator and the peripheral sealer and the thermal stress between the separator and the gas-distributor becomes the same, and the warp and the distortion at the time of calcination can be reduced. Such a situation is particularly favorable in the case where the separator and the electrode substrates are calcined into one body, and since in the peripheral region of the thin plate-like composite substrate, the peripheral sealer and the gas-distributor have been disposed and joined in face to face on the both surfaces of the separator while holding the separator, such a structure has a reinforcing effect, and as a result, the composite substrate according to the present invention is extremely excellent in the handling at the time of producing the fuel cell.

The composite substrate of the present invention, which is obtained as above, has the sum of the cross-sectional area of the flow channels of the reactant gas on the both electrode sides, which sum has been conformed with the conditions of the actually supplied reactant gas. Accordingly, as compared to the electrode substrate having the same sum of the cross-sectional area of the flow channels of the reactant gas on the fuel electrode side and on the air electrode side, the sum of the cross-sectional area of the flow channels of the - 31 reactant gas on the fuel electrode side can be reduced while maintaining the same performance at the time of operating the apparatus as a fuel cell. Namely, the height of the flow channels of the reactant gas can be lowered. Consequently, it is possible to make the thickness of the composite substrate itself thinner.

For instance, in the ordinary composite substrate of a thickness of from 3.8 to 4.0 mm, since the flow channels of the reactant gas are formed at the height of from 1.0 to 1.4 mm, the thickness of the electrode substrate can be made thinner by about from 0.6 to 0.9 mm at maximum, and as the whole substrate, the thickness can be reduced by about from 15 to 24 %. Such a construction not only contributes to the compaction of the fuel cell but also is able to reduce the electric resistance and thermal resistance by the same extent (from about 15 to 24 %) due to the reduction of the thickness of the composite substrate. Consequently, a higher fuel efficiency is expected to the composite substrate of the present invention.

Furthermore, in the composite substrate for fuel cells according to the present invention, since

the peripheral sealers has been joined to the extended peripheries of the separator in one body via the sheet of a fluorocarbon resin while being adjacent to the both edges of the electrode substrate, the composite substrate according to the present invention is excellent in preventing the gas-leakage, and it is not necessary to carry out the peripheral sealing treatment which is necessitated in the ordinary fuel cell for preventing the leakage of the reactant gas to the sides of the fuel cell.

Still more, the electrode substrates and the separator have been joined into one body via the flexible carbon sheet or have been joined by the dispersion of a tetrafluoroethylene resin, and the peripheral sealers and the separator have been joined into one body by the fluorocarbon resin. Accordingly, the composite substrate of the present invention is excellent in resistance to phosphoric acid and is particularly useful as the composite substrate for fuel cell of phosphoric acid type.

In addition, in the composite substrate of the present invention, since the peripheral sealers have been evenly disposed on and joined to the peripheral region of the thin plate-like composite substrate while holding the separator alternately in both sides, there is a reinforcing effect by such a construction, and as a result, the above-mentioned composite substrate is excellent in the handling at the time of producing the fuel cell.

The present invention will be explained more in detail while referring to the following Example, however, the scope of the present invention is not restricted by the following Example.

EXAMPLE:

The composite substrate for fuel cells according to the present invention was produced while using the following materials:

(1) *Electrode substrates:*

1-1: A porous and carbonaceous flat plate (made by KUREHA KAGAKU KOGYO Co., Ltd. under the trade name of KES-400) which had been preliminarily calcined at a temperature of not lower than 800°C in a nitrogen atmosphere and had the dimensions of 690 mm in width and length, respectively and 1.47 mm in thickness.

1-2: A porous and carbonaceous flat plate which is the same as that used in the above 1-1 except for having the thickness of 0.97 mm instead of the thickness of 1.47 mm.

(2) *Separator:*

The separator was obtained by cutting a compact carbon plate (made by SHOWA DENKO Co., Ltd. with the trade name of SG-2, of a thickness of 0.6 mm) into a piece of 690 mm in length and width, respectively.

(3) *Sheet of a fluorocarbon resin:*

Four pieces of the sheet of a fluorocarbon resin were obtained by cutting a TEFLON® sheet (made by NICHIAS Co., Ltd., of a thickness of 0.10 mm) in accordance with the size of the peripheral sealer.

(4) *Flexible carbon sheet:*

Two pieces of the flexible carbon sheet were obtained by cutting a GRAFOIL® (made by U.C.C., of a bulk density of 1.10 g/ml and a thickness of 0.13 mm) in accordance with the size of the joining surface (690 mm in length and 550 mm in width).

(5) *Peripheral sealers:*

5-1: Two pieces of a compact carbon plate (made by TOKAI Carbon Co., Ltd., of a bulk density of 1.85 g/ml) were cut into the size of 690 mm in length, 20 mm in width and 1.5 mm in thickness.

5-2: Two pieces of a compact carbon plate (the same as above) were cut into the size of 690 mm in length, 20 mm in width and 1.0 mm in thickness.

After applying an adhesive of a phenol resin series on one side of each of the two electrode substrates and on one side of each of the two GRAFOIL sheets, the thus applied adhesive was dried.

Thereafter, the joining surface of GRAFOIL was joined to the joining surface of the electrode substrate, except the surface to be faced to peripheries of the separator to which the peripheral sealer material is joined, under the conditions of a temperature of 140°C, a pressure of 10 kgf/cm²G and a pressure-retention time period of 20 min.

Then, the GRAFOIL-adhered surface of the electrode substrate, which was the porous and carbonaceous flat plate of 1.47 mm in thickness, was cut-processed to form a plurality of the parallel grooves with a rectangular cross-section of 1.0 mm in height and 2 mm in width at an interval of 4 mm by a diamond blade. In the same manner, the GRAFOIL-adhered surface of the electrode substrate, which was the porous and carbonaceous flat plate of 0.97 mm in thickness,

was cut-processed to form a plurality of parallel grooves with a rectangular cross section of 0.5 mm in height and 2 mm in width at an interval of 4 mm.

Thereafter, onto the remaining GRAFOIL surfaces of the thus processed materials, the above-mentioned adhesive was applied and dried. In the same manner, on the opposing surfaces of the separator the above adhesive was applied and dried.

Thereafter, each of the remaining GRAFOIL surfaces of the two electrode substrates was adhered to the opposing surface of the separator so that the plurality of the parallel grooves in one of the two electrode substrates were perpendicular to those in the another electrode substrate under the conditions of a temperature of 140°C, a pressure of 10 kgf/cm²G and a pressure-retention time period of 20 min, and the thus adhered materials were calcined at 2000°C in a nitrogen atmosphere.

After calcination, the parts of the electrode substrate, facing to peripheries of the separator to which the peripheral sealers are joined, were removed to expose the extended peripheries of the separator, and a TEFLON sheet was interposed between each of the peripheral sealers and the separator and the two materials were joined by melt-adhesion of the Teflon sheet at 350°C under a pressure of 20 kgf/cm²G for a pressure-retention time period of 20 min.

By the above-mentioned procedures, a composite substrate for fuel cells, which had a thickness of 3.3 mm, was obtained.

COMPARATIVE EXAMPLE:

In the same manner as Example except for using two pieces of the porous and carbonaceous flat plates of 1.47 mm in thickness as the electrode substrates and cut-processing both the GRAFOIL-adhered surfaces of the two electrode substrate to form a plurality of the parallel grooves having a rectangular cross-section of 1.0 mm in height and 2 mm in width at an interval of 4 mm thereon, a composite substrate for fuel cells was produced. The thickness of the thus produced composite substrate was 3.8 mm.

The results of measurement of the electric resistance and thermal resistance of the thus produced two composite substrates of the EXAMPLE and the COMPARATIVE EXAMPLE are shown in the following table.

TABLE

	Example	Comparative Example
Thickness (mm)	3.3	3.8
Electric resistance (mΩ·cm²)	15	18
Thermal resistance (m²·hour·°C/kcal)	34	40

As are clearly seen in TABLE, in the composite substrate for fuel cells according to the present invention, the electric resistance and the thermal resistance thereof were able to be reduced by about from 15 to 18 % as compared to those of the ordinary composite substrate by making the thickness of the composite substrate thinner.

CLAIMS

1. A composite substrate for fuel cells, comprising

(1) a separator,

(2) two porous and carbonaceous electrode substrates which have been respectively provided with a plurality of grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof, and have been joined to opposing surfaces of said separator so that said flow channels of the reactant gas in one of said electrode substrates are perpendicular to those in the another electrode substrate and said separator extends beyond both edges of said electrode substrate that are parallel to said flow channels of the reactant gas

in said electrode substrate and

(3) peripheral sealers joined to the extended peripheries of said separator, which extend beyond the both edges of said electrode substrate, via a layer of a fluorocarbon resin,

a ratio of the sum of the cross-sectional area of said flow channels of the reactant gas formed by said separator and the grooves of said porous and carbonaceous electrode substrate on the fuel electrode side to the sum of the cross-sectional area of said flow channels of the reactant gas formed by said separator and the grooves of said porous and carbonaceous electrode substrate on the air electrode side being from 1:3 to 2:3.

2. A composite substrate for fuel cells according to claim 1, wherein a flexible carbon sheet has been interposed between the joining surfaces of said porous and carbonaceous electrode substrate and said separator.

3. A composite substrate for fuel cells according to claim 2, wherein said flexible carbon sheet has been obtained by carbonising a composite material comprising carbon fibres of a mean length of not less than 1 mm and a binder and has a thickness of not more than 1 mm, a bulk density of from 0.2 to 1.3 g/ml, a compression strain rate of not more than 2.0×10^{-1} cm^2/kgf^* and a flexibility of not being broken in the case where being bent to the radius of curvature of 10 mm, in said flexible carbon sheet carbon lumps derived from said binder being dispersed within the matrix of said carbon fibres and restraining a plurality of said carbon fibres, said carbon fibres being slidably held to one another by the carbon lumps.

4. A composite substrate for fuel cells according to claim 3, wherein said flexible carbon sheet has been produced by compressing expanded graphite particles obtained by subjecting graphite particles of a particle diameter of not more than 5 mm to acid-treatment and further heating the thus acid-treated particles, and has a thickness of not more than 1 mm, a bulk density of from 1.0 to 1.5 g/ml, a compression strain rate of not more than 0.35×10^{-2} cm^2/kgf^* and a flexibility of not being broken in the case where being bent to the radius of curvature of 20 mm.

5. A composite substrate for fuel cells according to claim 1, wherein said porous and carbonaceous electrode substrates and said separator have been joined by a dispersion of a tetrafluoroethylene resin.

6. A composite substrate for fuel cells according to any preceding claim, wherein said porous and carbonaceous electrode substrate has a bulk density of from 0.3 to 0.9 g/ml, a gas-permeability of not less than 200 ml/cm^2.hour.mmAq and an electric resistivity of not more than 200 mΩ. cm after having been calcined at a temperature of not lower than 1000°C in an inert atmosphere and/or under a reduced pressure.

7. A composite substrate for fuel cells according to any preceding claim, wherein said separator is a compact carbon material having a bulk density of not less than 1.4 g/ml, a gas-permeability of not more than 10^{-6} ml/cm^2.hour.mmAq, an electric resistivity of not more than 10 mΩ.cm and a thickness of not more than 2 mm.

8. A composite substrate for fuel cells according to any preceding claim, wherein said peripheral sealer is a compact carbon material having a bulk density of not less than 1.4 g/ml and the gas-permeability of not more than 10^{-4} ml/cm^2.hour.mmAq.

9. A composite substrate for fuel cells according to any preceding claim, wherein said fluorocarbon resin has a melting point of not lower than 200°C.

10. A process for producing a composite substrate for fuel cells according to claim 2, which process comprises the steps of

(1) adhering a flexible carbon sheet to one surface of each of two porous and carbonaceous electrode substrates of a flat plate form without grooves and of prescribed dimension while using an adhesive,

(2) subjecting each of the adhering surfaces of said electrode substrates to cut-processing to form grooves forming flow channels of the reactant gas thereon so that a ratio of the sum of the cross-sectional area of said flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of said flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3,

(3) adhering the surfaces of said flexible carbon sheet remaining on the thus cut-processed surfaces of said electrode substrates to opposing surfaces of said separator so that the grooves in one of said electrode substrate are perpendicular to those in the another electrode substrate,

(4) calcining the thus adhered materials at a temperature of not lower than about 800°C in an inert atmosphere and/or under a reduced pressure, and

(5) joining peripheral sealers comprising a gasimpermeable compact carbon material to extended peripheries of said separator, which extend beyond the both edges of said electrode substrate that are parallel to said flow channels of the reactant gas therein, via a sheet of a fluorocarbon resin.

11. A process according to claim 10, wherein said porous and carbonaceous electrode substrate is selected from the group consisting of (1) a molded material obtained by molding a mixture of short carbon fibers, a binder and an organic granular substance into one body by heating under a pressure and (2) a calcined material obtained by calcining said molded material

of the above (1) in an inert atmosphere and/or under a reduced pressure.

12. A process according to claim 10, wherein said flexible carbon sheet has been obtained by carbonizing a composite material comprising carbon fibers of a mean length of not less than 1 mm and a binder and has a thickness of not more than 1 mm, a bulk density of from 0.2 to 1.3 g/ml, a compression strain rate of not more than 2.0×10^{-1} cm²/kgf* and a flexibility of not being broken in the case of being bent to the radius of curvature of 10 mm, in said flexible carbon sheet carbon lumps derived from said binder being dispersed in the matrix of said carbon fibers and restraining a plurality of said carbon fibers, said carbon fibers being slidably held to one another by the carbon lumps.

13. A process according to claim 12, wherein said flexible carbon sheet is obtained by molding a composite material comprising carbon fibers of a mean length of not less than 1 mm and a binder of a carbonizing yield of not less than 10 % by heating under a pressure and calcining the thus molded composite material at a temperature of not lower than 850°C in an inert atmosphere and/or under a reduced pressure.

14. A process according to claim 10, wherein said flexible carbon sheet is produced by compressing expanded graphite particles obtained by subjecting graphite particles of a particle diameter of not more than 5 mm to acid-treatment and further heating the thus acid-treated graphite particles, and has a thickness of not more than 1 mm, a bulk density of from 1.0 to 1.5 g/ml, a compression strain rate of not more than 0.35×10^{-2} cm²/kgf* and a flexibility of not being broken in the case where being bent to the radius of curvature of 20 mm.

15. A process according to to any one of claims 10 to 14 wherein said adhesive is a thermosetting resin selected from the group consisting of phenol resins, epoxy resins and furan resins.

16. A process according to any one of claims 10 to 15, wherein the conditions for joining said electrode substrate to said separator are the joining temperature of from 100 to 180°C, the press-pressure of from 1 to 50 kgf*/cm²G and the presstime period of from 1 to 120 min.

17. A process for producing a composite substrate for fuel cells according to claim 3, which process comprises the steps of

(1) applying a dispersion of a tetrafluoroethylene resin on opposing surfaces of a separator,

(2) joining by melt-adhesion each of grooved surfaces of two porous and carbonaceous electrode substrates to the prescribed position of the opposing surfaces of said separator applied with the dispersion so that the grooves in one of said electrode substrates are perpendicular to those in the another electrode substrate, said electrode substrates being respectively provided with a plurality of the grooves forming flow channels of the reactant gas on one side thereof and one flat surface on the other side thereof, the size of the grooves being such that a ratio of the sum of the cross-sectional area of said flow channels of the reactant gas on the fuel electrode side to the sum of the cross-sectional area of said flow channels of the reactant gas on the air electrode side is from 1:3 to 2:3, and

(3) joining peripheral sealers comprising a gasimpermeable compact carbon material to extended peripheries of said separator which extend beyond the both edges of said electrode substrate that are parallel to said flow channels of the reactant gas therein, via a sheet of a fluorocarbon resin.

18. A process according to claim 17, wherein said porous and carbonaceous electrode substrate is produced by calcining the molded material obtained by molding a mixture of short carbon fibers, a binder and an organic granular substance into one body by heating under a pressure.

19. A process according to claim 17 or 18, wherein the joining by melt-adhesion of said separator and said porous and carbonaceous electrode substrate is carried out at a temperature of not lower than about 270°C under a pressure of not lower than 1 kgf*/cm²G.

20. A process according to any one of claims 10 to 19 wherein said separator is a compact carbon plate showing the shrinkage on calcination of not more than 0.2% at the time when it is calcined at 2000°C in an inert atmosphere and/or under a reduced pressure.

21. A process according to any one of claims 10 to 20, wherein said sheet of a fluorocarbon resin has a melting point of not lower than 200°C.

22. A composite substrate for fuel cells constructed and arranged substantially as herein described with reference to and as illustrated in the accompanying drawings.

23. Process of producing composite substrates for fuel cells, such processes being substantially as herein described with reference to the accompanying drawings.

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